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SOLID PARTICLE FORMATION
MECHANISMS

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The objective of this study is to identify the parameters which control the formation and growth of solid, non-spherical particles, specifically the formation of metallic fibers in magnetic fields and platelet particles in flames. The influence of hydrodynamic and magnetic forces are discussed. It is shown that materials with high entropy of phase transition exhibit selective morphological growth, while materials with low entropy of phase transition exhibit random, amorphous growth. Natural convection has the effect of increasing the temperature or concentration gradients near growing crystal interfaces. It thus has the effect of increasing heat and mass transport at the crystal surface. As the convective hydrodynamic forces increase, the growth mechanism changes from diffusion-controlled to kinetic-controlled with the net effect that particles grow isotropically. The application of magnetic fields to ferromagnetic particles induces particle-particle interactions, and the chaining of the primary particles to form non-spherical particles with large aspect ratios.

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FOREWORD

The results of a Short Term Analysis Study (STAS) of the phenomenology underlying crystal growth are presented. The study objective was to identify the parameters which control the formation and growth of solid, non-spherical particles, specifically the formation of metallic fibers in magnetic fields and platelet particles in flames.

The specific tasks performed included the assessment of crystal growth from liquid solution and the vapor phase (both without and with chemical reaction) with regard to the thermodynamic correlations and the influence of the hydrodynamics and magnetic fields. The reactivity of the particles, formed as a function of size, material and composition of the ambient atmosphere, was also assessed.

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PREFACE

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CONTENTS

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SOLID PARTICLE FORMATION MECHANISMS

INTRODUCTION

Knowledge of the mechanisms by which solid particles form from various fluid media opens the way for tailoring the process variables to produce particles of desired sizes and shapes. Although a great deal of information exists in the literature on mechanisms of formation of specific material particles, a general practical guide for the production of solid particles of specific sizes and shapes is lacking. This document attempts to remedy this situation by presenting an overview, as assessed from current literature, of solid particle formation phenomenology. The cases of formation of micron size particles from solution and vapor (without and with chemical reaction) media are then considered in more detail. The effects of magnetic fields during growth are also considered as are some aspects of particle oxidation after formation.

GENERAL PHENOMENOLOGY OF CRYSTAL GROWTH

Rate Phenomena

The sizes and shapes of crystals formed from a fluid phase is determined by the interplay of three basic processes: nucleation, crystal growth, and material and heat transport. The following is a general overall description of the interplays in the case of crystal growth from the melt.

To initiate the formation of a solid phase from a liquid phase solid nuclei must form a large enough size (critical size) that further growth decreases the free energy of the system. The rate at which such nuclei form is a function of supercooling, generally as shown by curve A in Fig. 1.
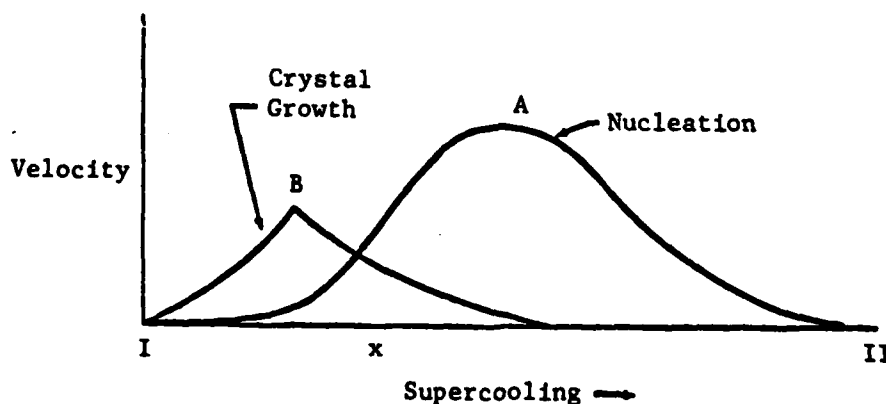

Fig. 1 Crystal Growth and Nucleation Rates as a Function of Supercooling

The rate of crystal growth subsequent to nucleation is generally as shown by curve B in Fig. 1.

The initial increase in rate as the supercooling increases is the result of an increased thermodynamic driving force for phase change. The subsequent decrease in rates at extreme supercooling is the result of increased activation energies as made manifest by increased viscosity.

Depending on the particular degree of supercooling, a variety of outcomes can occur. If the rate of nucleation is relatively high and the crystal growth rate low, a shower of minute crystals can result. On the other hand, if the rate of nucleation is relatively low and the rate of crystal growth high, a few large crystals can be the result.

The overall rate of crystal growth, once nucleation occurs, is determined by the relative rates of the atomic attachment processes or interface kinetics and the rate of heat or mass transport. For example, consider a crystal growing in a melt. As the crystal grows, latent heat of fusion is liberated which has to be removed if the crystal is to grow further. If the rate of heat removal is slower than the rate at which the atomic attachment processes can occur, the interface temperature remains just a little below the equilibrium phase change temperature because latent heat is being liberated fast enough to replace that lost by transport. The overall rate of phase change can be said to be heat-controlled. If, on the other hand, the rate of the atomic attachment processes is low while that of heat or mass transport is high, the interface temperature falls considerably below the equilibrium phase change temperature. The overall rate of phase change in such a case can be said to be kinetically controlled.

A semi-quantitative guide to whether a process is kinetically controlled or heat controlled was presented by W.B. Hillig (Ref. 1) in 1959. Hillig's treatment yields an α factor which is defined by the relationship:

$$\alpha = (1 + \frac{U}{V})^{-1}$$

where U is the crystal growth rate assuming total kinetic control, i.e., the
temperature of the solid-liquid interface, T_i, is assumed equal to the
ambient or reservoir temperature, T_∞. V is the crystal growth rate assum-
ing that the rate is totally determined by the heat flow rate, i.e., T_i is
equal to the solid-liquid equilibrium temperature, T_e. Approximate ex-
pressions for these two terms are:

$$U = \frac{\lambda 3 \, f \, D \Delta S_f \, (T_e - T_\infty)}{\lambda^2 \, RT}$$

$$V = \frac{gK}{\Delta H_f X} \, (T_e - T_\infty)$$

$$\frac{U}{V} = M = \frac{3 f D \Delta S_f \Delta H_f X}{\lambda R T_\infty g K}$$

where:

f   = fraction of molecules having the proper orientation to in-
corporate into the crystal

D   = the self-diffusion coefficient

ΔS_f = molar entropy of fusion

ΔH_f = enthalpy of fusion per square centimeter

λ^2 = an area of molecular dimension

T_∞ = temperature of thermostat

T_e = equilibrium phase change temperature

K   = mean thermal conductivity

X   = characteristic length for the advancing interface

g   = constant of the order of unity which depends on the geometry of
the system.

The   factor assumes values of >0.9 for kinetically controlled processes and
<0.1 for heat transport processes. The M factor furthermore gives some in-
formation about the types of materials that can be shown kinetically con-
trolled. Hillig sets the conditions that M≤1 for a kinetic process to be
observed at all. M can be·shown to be approximately equal to $10^6 f(D/K)$,
where f is the fraction of molecules having the proper orientation to incor-
porate into the crystal, D is the self-diffusion coefficient, and K is the
mean thermal conductivity of the material. The M factor for various
materials is summarized in Table 1.

Table 1   CALCULATED M VALUES FOR VARIOUS MATERIALS

Metals	$10^{2.5} f$
Water	$10^4 f$
Ionic Melt	$10^4 f$
Viscous Ionic Melt	<1

The M values given in Table 1 indicate that the crystallization of a viscous
ionic melt would be expected to generally be kinetically controlled, while
the crystallization of the other materials would generally be expected to be
heat-controlled.

Material Factors

Shapes or morphologies of crystalline particles are determined both by
the rate-controlling process and by the nature of the material itself. The
statistical mechanical treatment of Jackson and Chalmers (Ref. 2) of the
atomic attachment processes gives an insight into the role of the material
in determining crystalline morphology. According to Jackson and Chalmers,
when additional molecules are added randomly to an initially plane surface
at its equilibrium temperature T_e, the change in free energy is given by:

$$\frac{\Delta F}{NkT_e} = \alpha x(1 - x) + x \ \ln x + (1 - x) \ln (1-x)$$

13

where

$$\alpha = \frac{\Delta L}{RT_e} = \frac{\Delta S}{R} \xi$$

The terms in the above expressions are identified as:

x = fraction of the N possible sites on an initially plane face

k = Boltzmann constant

ΔL = latent heat of transformation

R = gas constant

ΔS = entropy of transformation

ξ = fraction of the total binding energy which binds a molecule in a layer parallel to the plane face to other molecules in the layer. The factor is always less than unity and is largest for the most closely packed planes. For these it is invariably greater than or equal to 0.5.

A plot of $\Delta F/NkT_e$ vs x for different values of α is shown in Fig. 2.
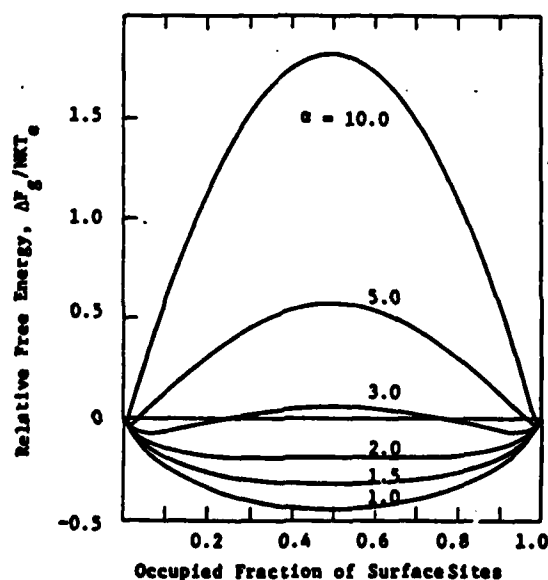

Fig. 2 Free Energy of an Interface vs Occupied Fraction of Surface Sites (after Jackson)

14

For α < 2, the lowest free energy configuration corresponds to half the available sites filled and thus may be taken as a rough interface on an atomic or microscopic scale. For α > 2, few molecules are missing from the completed layer, and thus this case may be taken as a smooth interface.

The effect of undercooling is to change the curves so that faces which are smooth at equilibrium may become rough at some large undercooling. For most materials, however, the effect of undercooling is to shift the maxima slightly.

For materials with $\Delta S/R < 2$, even the most closely packed planes should be rough, and the initiation of new layers relatively easy. On an atomic scale, the interface will be rough. Rough interfaces, exhibiting as they do, low energetic barriers to growth, tend generally to have transport-controlled growth rates. Low $\Delta S/R$ materials will thus tend to exhibit non-faceted morphologies and little growth rate anisotropy. For $\Delta S/R > 4$, the most closely packed faces should be smooth, and the initiation of new layers difficult. Less closely packed faces are expected to be rough. Materials with high $\Delta S/R$ will tend to show faceted morphologies, sizeable growth rate anisotropy, and kinetically controlled growth rates.

Materials of intermediate $\Delta S/R$ values would be expected to show either non-faceted and faceted morphology depending on the actual conditions of growth.

Particle Morphologies and Conditions of Growth

The question of crystal morphology as a function the rate-controlling process is rather complicated because the growth mechanisms and growth rates of the separate crystal faces as a function of undercooling are generally not known. Rather elaborate rate studies are required to specify a particular sequence for a particular material. However, the following generalization can serve to indicate general tendencies.

For growth from the melt, the following sequence of morphologies as a function of undercooling occurs for materials of low $\Delta S/R$ and under condition of heat-control (Ref. 3).

Dendrite   Spherulite

Undercooling Increasing
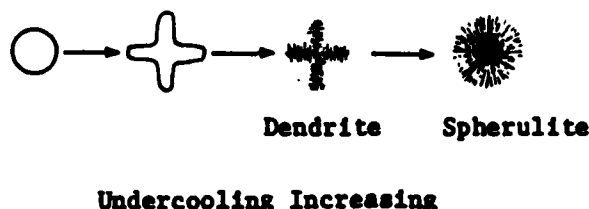
The spherulite morphology is generally thought to be the result of the large undercooling producing such a high density of needles that the thermal fields of each overlap suppressing side branching.

Materials of high $\Delta S/R$ generally show anisotropic growth. In such cases the fastest growing face will soon be grown out leaving a crystal bounded by the slowest growing faces. The differences in growth rates of the various faces may be the result of: (1) intrinsic differences because of different molecular forces in different crystal plane; or of (2) the occurrence of a screw dislocation on certain faces which makes growth on those faces much easier than on other faces; or (3) the occurance of a twin crystal, or (4) preferential absorption of impurities on certain crystal faces, retarding or enhancing growth on those faces. For high entropy materials and heat-control conditions the following sequences of morphologies as a function of undercooling can be projected:

Dentrites   Spherulites

Undercooling Increasing

16
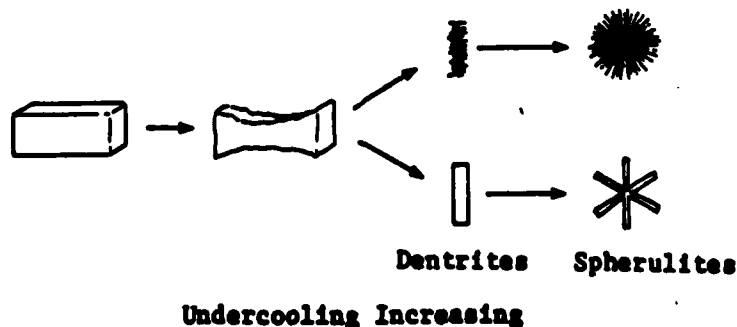
Under kinetically controlled conditions high entropy materials would be expected to show the following sequences:

Whisker,
Undercooling Increasing
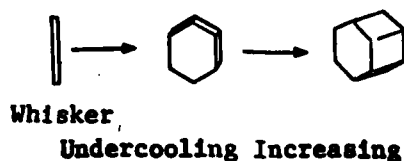
In this case the needle or whisker, morphology is generated as the result of a screw dislocation mechanism on one face of the crystal causing a faster growth in one direction. As the undercooling increases two-dimensional nucleation increases, causing the other faces to increase their growth rates.

Recently a couple of works (Refs. 4 and 5) have expanded the concept of a controlling entropy term to include the cases of crystal growth from solution, from vapor, and from solid media. In the treatment of Bourne and Davey (Ref. 4), a surface entropy factor, α, is taken as the definitive parameter. The surface entropy factor, α, is defined by these authors as follows:

$$\alpha = 4 \, \Upsilon/kT$$

where Υ is the edge energy or the energy gain upon the creation of a solid-fluid bond. For qualitative purposes α can be taken as:

$$\alpha = \frac{n_s}{n_{ot}} \, \frac{\Delta S}{R}$$

where ΔS is the entropy of phase transition and n_s and n_t the number of nearest neighbors parallel to the crystal surface and in the bulk crystal respectively. The appropriate entropy terms for the cases of crystal growth from solution and vapor are as follows:

Case	Entropy Term

Growth from Solution   Entropy of Solution
                            $\Delta S = \Delta S_F + \Delta S_M$

Growth from Vapor $\Delta S = \Delta S_{Sub}$

where the entropy terms ΔS_F, ΔS_M and ΔS_{Sub} are for the processes of fusion, mixing and sublimation.

In this treatment rough interfaces are characterized by α values of 3.2 or less and smooth interfaces by α values of greater than 4. Furthermore, because the energy gain upon the creation of a solid-fluid bond at the interface is a function of solvent-solute interactions, the value of λ may have different values for different solvents. Thus a given face of a crystal may grow by different growth mechanisms from different solvents.

In another study, B. Lewis (Ref. 5) defines an edge energy coefficient β for crystal growth from solution as:

$$\beta \simeq \Delta H_S - 2\rho \quad T\Delta S_s \quad 2\rho$$

where ΔH_S is the enthalpy of solution, ΔS_S the entropy of solution, and ρ is the surface energy. Lewis' analysis leads to the conclusion that β is the primary material parameter for two-dimensional nucleation (2DN) and also for screw dislocation (SDG). When $\beta/kT>10$ which is typical of growth from the vapor on low energy plans, 2DN is slower than SDG. When $\beta/kT<8$, which is typical of melt growth, 2DN is faster than SDG at moderate supercooling and slower at low supercooling. When $\beta/kT \lesssim 2$, growth by either mechanism is unimpeded at all supersaturations.

In earlier studies of whisker formation (Refs. 6 through 9) Sears found that whisker growth occurs only when the supersaturation ratio remains below

a critical value, which is determined by the supersaturation at which two-dimensional nucleation occurs. Sears postulates that a nucleus with a built-in screw dislocation grows axially at low supersaturation by the action of the dislocation with absorbed atoms feeding the growth. Radial growth, however, cannot occur because the supersaturation is below the critical value for two-dimensional nucleation.

Lewis[*] work indicates that materials of $\beta/kT>10$, i.e., materials with high entropy of phase transition, readily form whisker and platelets over a wide range of processing parameters. Materials of lower β/kT will require careful adjustment of processing parameters such as the supersaturation to effect whisker or platelet formation.

The cited studies described in the preceding discussion has prompted the use of model materials to verify or to illuminate some points of crystal growth either for theoretical or practical purposes. For example, organic materials of low melting points, low entropies of fusion, and transparent melts have been taken as models for crystallization of metals from the melt (Ref. 9). Solutions of ammonium chloride in water have been studied as models for crystallization phenomena in alloy castings (Ref. 10). The model materials work has been exceptionally fruitful in explaining and elucidating many processes involved metal crystallization.

The entropy of phase transition also plays a role in nucleation kinetics. For purposes of the present study it is sufficient to note materials with high entropies of phase transition are generally difficult to nucleate and will require either extreme supercooling, supersaturation, seeding, or catalysts to effect.

Convection Effects on Crystal Growth

Natural convection has the effect of increasing the temperature or concentration gradients near growing crystal interfaces. It thus has the effect of increasing heat or mass transfer to growing crystal surfaces.

This increased mass or heat transport can affect crystal growth in a variety of ways. The increased gradients can not only increase crystal growth rate, but also, in certain cases, change the controling process from heat or mass transfer to that of kinetic-control. The crystal morphologies will thus then to change from dendrite to more three-dimensional, particle-like structures. In the case of the kinetically-controlled process of whisker growth, convection currents can increase the mass flow to the side of the crystal, encouraging a thickening of the crystal by 2-D nucleation. In the absence of convection, i.e., the pure diffusion case, less mass would reach the sides and more the ends of the whiskers, thus encouraging growth lengthwise.

Natural convection can also introduce areas of nonuniform temperatures or concentrations along the growing crystal surface and can thus lead to a number of crystalline defects.

Conclusions

On the basis of the preceding discussion, the following generalization for growing micron sized particles of specified shapes are drawn. Materials with high entropy of phase transition can be expected to be easily grown in the specified morphologies, particularly from the vapor or solution phases. Materials with lower entropies of phase transition possibly can be grown to the specified shapes by carefully controlling the processing parameters.

GROWTH FROM SOLUTION

As a crystal grows from solution it depletes solute in the solution
adjacent to the growing crystal surface, thereby creating a concentration
gradient. The concentration gradient provides the driving force for species
diffusion toward the growing interface. If the interface kinetics are fast
enough, compared to the transport processes, the surface concentration
equals the solubility of the crystal or C_e. If the interface kinetics are
slow compared to the transport processes, the surface concentration will be
higher than C_e, approaching C_f, the concentration in the bulk of the
solution, in cases of very slow interface kinetics. Heat effects accompany-
ing the crystallization can usually be ignored because the diffusivity of
heat in solution is so much larger than the diffusion of solution species.

In crystal growth from solution, the rate of nucleation increases
extremely rapidly with a small increase in supersaturation beyond the
"metastable region." Furthermore crystals of highly soluble compounds are
grown with great ease, while slightly soluble compounds are grown with great
difficulty. Also, the maximum rate at which growth without propagation of
flaws can be obtained decreases as the size of the crystal surface
increases. This critical growth rate increases with increasing temperature.

These characteristics of solution growth mean generally that profuse
amounts of small crystals of polyhedral shapes can be easily obtained while
large perfect crystals are hard to obtain. One notable feature of crystal
growth from solution is that the crystal morphologies can be easily changed
by the addition of impurities or by a chain of solvent.

CRYSTAL GROWTH FROM THE VAPOR PHASE
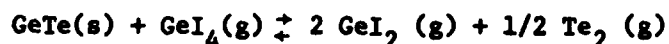
Without Chemical Reaction

Numerous reports exist of the growth of fine metal crystallites from the vapor. Of particular interest to the present study are reports on the technique of evaporating a metal in an atmosphere of inactive gas such as He, Ar, or Xe. With such a technique it is possible to form clouds of smoke directly (Refs. 11, 12, and 13). Studies on Fe, Zn, Mn, Be, Mg, Co and others have been performed by this technique. The crystalline structures produced by this technique are generally polyhedra with some instances of platelets and rods. Particles of ferromagnetic material made by this technique often, but not always, display remarkable "necklace-like arrangements" (Ref. 14).

The prediction that materials with similar entropies of transition show similar crystallization behavior finds support in the data reported in these studies. A number of instances are reported where the morphologies of the metal particles are similar to those found in snow. Also the morphologies of the particle could be changed drastically by the addition of a small amount of another gas such as oxygen. For Be, Mg, Zn, and Cd the structure became very rough and irregular, while for Fe, Mg, and other similar metals the metals became smooth and nearly circular. The latter behavior strongly suggests that adsorption of oxygen species on the growing crystallites increased the rate of the intrinsic kinetic processes.

With Chemical Reaction

Growth of crystals from a vapor phase which is chemically reactive is really not much different from the case of crystal growth from the vapor

22

without chemical reaction. The only difference is that some sort of chemical reaction must precede the crystal growth. For example, the semiconductor crystal germanium telluride can be grown utilizing the reaction:

$$GeTe(s) + GeI_4(g) \rightleftharpoons 2 GeI_2 (g) + 1/2 Te_2 (g)$$

Source GeTe(s) is reacted with GeI_4 (g) at the hot end of a reaction tube producing the gases GeI_2 and Te_2. These gases transport to the cold end of the tube where they interact to deposit single crystal GeTe.

If the rate of chemical reaction is fast compared to the diffusion and crystal growth processes, then the chemical reaction itself plays a minor role in the subsequent crystal growth processes. For example, in the case of GeTe it was found that the morphology of GeTe particles was affected primarily by the transport processes (Ref. 15). Diffusive transport yielded predominately octahedral type crystals, while convective flows received mainly platelet type crystals with random imperfections, growth spirals, and station patterns. These results are in keeping with the morphology sequence given on page 9 for high entropy materials under diffusion control. Convection has the effect of thinning the diffusion boundary layer next to the crystal surface thereby increasing the supersaturation.

Related to the growth of crystals from the vapor by chemical reaction is the growth of iron whiskers by reduction of solid ferrous chloride by a hydrogen stream (Ref. 16). In this case the rate is limited by the rate of halide vapor adsorption at the growth site of the growing whisker. The addition of carbon black to the ferrous chloride results in a profusion of whiskers (Ref. 17). The carbon black particles act to increase the heat of adsorption of halide vapor resulting in increased nucleation rate.

In cases of whisker growth from the vapor phase, with or without chemical reaction, it was found that the presence of additional gases can exert profound effects on crystal morphology.

EFFECTS OF MAGNETIC FIELDS

Discussion of the effect of magnetic fields on crystal growth requires the recognition that the magnetic field in question may be internally or externally generated. Internally generated fields are caused by the particles of interest themselves. For example, iron particles of an appropriate size (~ 150Å) are ferromagnetic and thus attract each other to form chain-like necklaces when they are formed by deposition from the vapor phase (Ref. 18). One study of the formation of iron sulfide particles found that chains occur far from the evaporation source and can be composed of different shaped particles, depending on the pressure during evaporation (Ref. 19). If a magnetic field is applied during the formation of chains, the chains arranged themselves parallel to the applied field.

OXIDATION OF SMALL METAL PARTICLES

Most metal particles rapidly acquire an oxide film. The film, however, usually reaches a limiting film thickness which is characteristic of the particular surface and temperature. In the case of iron powder produced from the carbon and annealed in hydrogen, an oxide film of the order of 20 Å develops in the first few minutes after exposure to the atmosphere (Ref. 20). The film increases to 35 Å after 100 hr. Small particles of Fe-Co alloy (~150 Å) in diameter were subjected to an accelerated aging test in another study (Ref. 21) These particles were kept at 95% humidity and 40 C for ten days, which is considered to correspond to an aging for two years in the open air. The saturation magnetization of the particles shows no detectable change. This stability is attributed to protection by preexisting surface oxide layers. The presence of the oxide layer, however, reduced the magnetization to about 80 percent of those of the bulk metals.

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